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A μ-Pyrazolyl Terpyridineplatinum(II) Dimer

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Abstract. μ-(Pyrazolyl-*N*:*N'*)-bis[(2,2',2''-terpyridine)platinum(II)] perchlorate acetonitrile solvate, $[Pt_2(C_{15}H_{11}N_3)_2(C_3H_3N_2)](ClO_4)_3.CH_3CN$, M_r = 1263.18, orthorhombic, *Pnma*, $a = 18.172$ (2), b = 17.950 (3), $c = 12.086$ (4) Å, $V = 3942.3$ (15) Å^3, Z = 4, $D_x = 2.128$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 74.41 cm^{-1}, $F(000) = 2416$, room temperature (297 K), $R = 0.0337$ for 2510 reflections with $F_o^2 > 3\sigma(F_o^2)$. A single pyrazolyl unit bridges two Pt centres. The square-planar coordination around each Pt atom is completed by a tridentate terpyridine ligand. The Pt···Pt separation is 3.432 (1) Å with an inclination of 47.7 (12)° between the two Pt square planes.

Introduction. We are currently investigating the properties of binuclear terpyridineplatinum(II) complexes. The compound (μ-pz)bis[(tpy)Pt](ClO$_4$)$_3$ (pz = pyrazolyl, tpy = terpyridine) is one of a series of binuclear complexes that have been synthesized in which the interplatinum distance is varied. The effect of the Pt-atom separation on absorption and emission spectra can be readily studied with these complexes.

Experimental. This material was synthesized by heating an aqueous solution of [Pt(tpy)Cl]Cl and pyrazole (1/2 equiv.) (pH adjusted to *ca* 9 with 1*M* NaOH) to 348 K for 5 d. The orange–red solution slowly changed to pale orange. Cooling and addition of NaClO$_4$ precipitated the product as a perchlorate salt. Crystals for X-ray analysis were grown by slow evaporation of an acetonitrile solution. A pale orange tabular block crystal 0.22 × 0.42 × 0.60 mm was used for data collection on a CAD-4 diffractometer, with ω-scan technique. 25 reflections with $34 < 2\theta < 41°$ were used for determination of the cell dimensions. An empiricial absorption correction based on ψ scans of six reflections, with relative transmission from 0.508 to 1.388, was applied. $(\sin\theta/\lambda)_{max} = 0.54$ Å^{-1}; h from −14 to 14, k from −21 to 21, l from 0 to 17. Three standard reflections (153, 411, $\bar{3}42$) showed decay of 0.6% in 148 h of data collection; data were corrected for this decay. 14841 reflections were measured, of which 3588 were independent. Goodness of fit for merging was 1.35 (R_{merge} for 378 reflections with exactly two observations, 0.0175). All reflections were used in solution and refinement of the structure. Coordinates of the Pt atom were found from a Patterson map, remaining heavy atoms were found by successive structure factor – Fourier calculations, including an acetonitrile molecule of crystallization and two perchlorate ions. F_o^2 magnitudes were used in full-matrix least-squares refinement, which minimized $\sum w(F_o^2 - F_c^2)^2$. H atoms were positioned by calculation (C—H = 0.95 Å) and included as constant contributors to the structure factors. H atoms on the acetonitrile were calculated for two possible positions based on the symmetry of the mirror plane which contains the CH_3CN molecule; difference and Fourier maps did not favor either conformation so both positions were included, each contributor being set at half occupancy. H-atom parameters were not refined but recalculated once, near the conclusion of the refinement. Positional and anisotropic temperature parameters for all non-H atoms (except O in disordered ClO_4^-, isotropic), a scale factor and secondary-extinction parameter were refined. At convergence, difference maps suggested that the second ClO_4^- ion which occupies a special position on a mirror plane might be modeled more appropriately as the superposition of two ions each with half occupancy and sharing both the Cl2 and O6 positions. Although this model accounts for most of the electron density in the area and the average Cl—O bond length is 1.43 Å, the actual bond lengths and angles deviate substantially from a tetrahedral ClO_4^- geometry; however, other disorder models did not improve on this result, so refinement was terminated at this stage.

$R = 0.0514$ for 3346 reflections with $F_o^2 > 0$, wR (on F^2) = 0.0050 and goodness of fit = 2.01 for 3588 reflections and 293 parameters. Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error

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Table 1. *Final refined atomic coordinates* ($\times 10^4$) *and equivalent isotropic* ($Å^2 \times 10^4$)*/isotropic* ($Å^2$) *temperature factors for* μ*-pyrazolyl terpyridineplatinum dimer*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}/B†
Pt	769 (.1)	1544 (.1)	773 (.2)	436 (1)
N1	1651 (3)	2128 (3)	1306 (4)	519 (14)
N2	221 (3)	1425 (3)	2227 (5)	531 (16)
N3	−97 (3)	1032 (3)	230 (5)	482 (15)
N4	1067 (3)	1445 (3)	−829 (5)	550 (16)
C1	2318 (4)	1911 (4)	1652 (7)	742 (26)
C2	2745 (5)	2500	1840 (10)	676 (33)
C3	443 (4)	1620 (5)	3238 (6)	619 (20)
C4	10 (5)	1515 (5)	4129 (7)	777 (25)
C5	−681 (5)	1190 (5)	4040 (7)	756 (26)
C6	−899 (4)	966 (5)	3011 (7)	670 (23)
C7	−447 (4)	1081 (4)	2096 (6)	519 (19)
C8	−630 (3)	874 (4)	965 (6)	501 (21)
C9	−1271 (4)	542 (4)	570 (8)	653 (24)
C10	−1347 (4)	426 (5)	−521 (8)	710 (24)
C11	−797 (5)	604 (5)	−1273 (7)	746 (25)
C12	−153 (4)	920 (4)	−872 (6)	518 (20)
C13	511 (5)	1127 (4)	−1465 (7)	596 (23)
C14	631 (5)	993 (5)	−2565 (8)	804 (27)
C15	1319 (7)	1148 (6)	−3024 (8)	899 (31)
C16	1856 (5)	1429 (5)	−2375 (9)	878 (29)
C17	1725 (4)	1580 (4)	−1281 (7)	667 (21)
Cl1	1776 (1)	169 (1)	3969 (2)	637 (5)
O1	1012 (3)	12 (3)	3858 (5)	844 (17)
O2	1883 (3)	920 (3)	4340 (5)	933 (19)
O3	2096 (3)	−323 (4)	4753 (5)	1018 (20)
O4	2142 (3)	103 (4)	2928 (5)	985 (19)
Cl2	3943 (2)	2500	8099 (3)	971 (12)
O5	4294 (11)	2500	6855 (18)	9.7 (6)†
O6	4620 (10)	2500	8521 (14)	17.9 (6)†
O7	3500 (12)	2097 (12)	7490 (17)	16.4 (7)†
O8	3366 (14)	2500	9120 (19)	11.9 (7)†
O9	3944 (9)	1774 (11)	8288 (14)	10.8 (5)†
N5	3957 (8)	2500	4114 (13)	1237 (50)
C18	2712 (9)	2500	5083 (12)	1037 (49)
C19	3412 (9)	2500	4573 (12)	837 (43)

† Isotropic displacement parameter.

Table 2. *Selected distances* (Å) *and angles* (°) *for* μ*-pyrazolyl terpyridineplatinum dimer*

Pt—N1	2.020 (5)	Pt—N2	2.031 (6)
Pt—N3	1.938 (5)	Pt—N4	2.018 (6)
N1—C1	1.340 (9)	N1—N1	1.335 (7)
N2—C3	1.334 (10)	N2—C7	1.370 (9)
N3—C8	1.345 (9)	N3—C12	1.350 (9)
N4—C13	1.391 (10)	N4—C17	1.337 (10)
C1—C2	1.331 (13)	C3—C4	1.347 (12)
C4—C5	1.388 (13)	C5—C6	1.366 (12)
C6—C7	1.393 (11)	C7—C8	1.456 (10)
C8—C9	1.392 (11)	C9—C10	1.342 (12)
C10—C11	1.389 (12)	C11—C12	1.388 (11)
C12—C13	1.451 (11)	C13—C14	1.370 (12)
C14—C15	1.395 (14)	C15—C16	1.349 (14)
C16—C17	1.371 (13)		
N2—Pt—N1	99.7 (2)	N3—Pt—N1	177.0 (2)
N4—Pt—N1	98.0 (2)	N3—Pt—N2	81.1 (2)
N4—Pt—N2	162.2 (2)	N4—Pt—N3	81.4 (2)
C1—N1—Pt	131.8 (5)	N1—N1—Pt	121.3 (4)
N1—N1—C1	106.9 (5)	C3—N2—Pt	128.1 (5)
C7—N2—Pt	112.5 (4)	C7—N2—C3	119.4 (6)
C8—N3—Pt	117.5 (4)	C12—N3—Pt	117.7 (4)
C12—N3—C8	124.5 (6)	C13—N4—Pt	111.8 (5)
C17—N4—Pt	128.0 (5)	C17—N4—C13	119.9 (6)
C2—C1—N1	110.5 (8)	C1—C2—C1	105.1 (9)
C4—C3—N2	121.3 (7)	C5—C4—C3	121.7 (8)
C6—C5—C4	117.2 (8)	C7—C6—C5	120.5 (7)
C6—C7—N2	119.9 (6)	C8—C7—N2	115.2 (6)
C8—C7—C6	124.9 (7)	C7—C8—N3	113.7 (6)
C9—C8—N3	117.8 (6)	C9—C8—C7	128.5 (7)
C10—C9—C8	119.3 (7)	C11—C10—C9	122.2 (8)
C12—C11—C10	118.2 (8)	C11—C12—N3	117.9 (7)
C13—C12—N3	112.8 (6)	C13—C12—C11	129.3 (7)
C12—C13—N4	115.8 (7)	C14—C13—N4	119.5 (7)
C14—C13—C12	124.6 (7)	C15—C14—C13	119.6 (8)
C16—C15—C14	119.4 (9)	C17—C16—C15	120.6 (9)
C16—C17—N4	120.8 (8)		

plus another additional term, $(0.014\bar{I})^2$. In the final least-squares cycles $(\Delta/\sigma)_{max} = 0.04$; $-0.91 \le \Delta\rho \le 1.57$ e $Å^{-3}$ in the final difference Fourier map, with all large peaks within 1.5 Å of the Pt atom. Atomic scattering factores and values for f' were taken from Cromer & Waber (1974) and Cromer (1974). Programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEP*II (Johnson, 1976). Final atomic coordinates and U_{eq} are listed in Table 1 with selected distances and angles given in Table 2.*

Discussion. Fig. 1 shows the cation viewed along the intermetal axis with atom labels; Fig. 2 is a stereoscopic view of the entire 3+ cation. The geometry around the Pt atoms is nearly square planar, distorted only by the restricted bite angle of the planar

* Lists of assigned H-atom parameters, complete distances and angles, anisotropic temperature parameters and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55055 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0585]

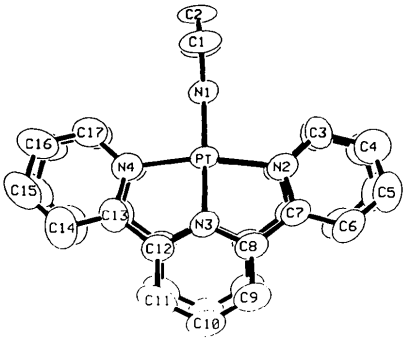

Fig. 1. A labeled *ORTEP*II (Johnson, 1976) drawing of the cation with 50% probability ellipsoids viewed down the intermetal axis. H atoms are not shown.

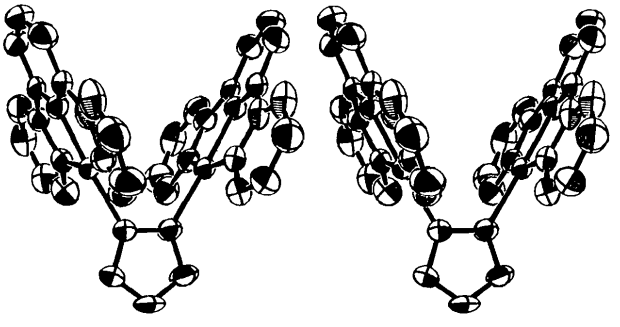

Fig. 2. An *ORTEP*II (Johnson, 1976) stereoscopic drawing showing the complete cation. Atoms are shown as 50% probability ellipsoids.

terpyridine unit. This results in a short Pt—N3 distance [1.938 (5) Å] and an N2—Pt—N4 *trans* bond angle of only 162.2 (2)°. The remaining bond lengths around the Pt atom are all over 2 Å [2.018 (6), 2.020 (5) and 2.031 (6) Å]. This geometry is entirely consistent with other related Pt(tpy) complexes (Dewan, Lippard & Bauer, 1980; Ratilla, Scott, Moxness & Kostic, 1990; Wong & Lippard, 1977; Jennette, Gill, Sadownick & Lippard, 1976).

The two Pt atoms are bridged by a single pyrazolyl group, resulting in a Pt···Pt separation of 3.432 (1) Å (parallel, by symmetry, with the *y* axis) and an inclination between the two square planes of 47.7 (12)°. This distance is intermediate in the range of $Pt^{II}\cdots Pt^{II}$ separations exhibited by other binuclear tpy complexes, that have been observed as short as 2.9884 Å (Ratilla *et al.*, 1990) and as long as 4.420 Å (Dewan *et al.*, 1980). The Pt atom is displaced out of the terpyridine plane by *ca* 0.2 Å towards the other Pt atom in the same binuclear unit. The bond lengths and angles within each pyridine ring are characteristic of a delocalized aromatic system, ranging from 1.334 (10) to 1.395 (14) Å and from 117.2 (8) to 124.9 (7)°. Similarly, the bond lengths and angles within the pyrazolyl ring range from 1.331 (13) to 1.340 (9) Å and from 105.1 (9) to 110.5 (8)°, thereby demonstrating the delocalized nature of the π electrons in the five-membered ring.

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Structure of (Benzenethiolato)oxo[*N*-(2-sulfidophenyl)salicylideneiminato(2−)-*O,N,S*]technetium(V)*

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Abstract. $[Tc(C_{13}H_9NOS)(O)(C_6H_5S)]$, $C_{19}H_{14}NO_2S_2Tc$, $M_r = 451.2$, monoclinic, $P2_1$, $a = 7.901$ (1), $b = 10.147$ (1), $c = 11.370$ (2) Å, $\beta = 93.60$ (1)°, $V = 909.8$ (2) Å^3, $Z = 2$, $D_x = 1.646$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1$ mm^{-1}, $F(000) = 452$, $T = 293$ K, $R = 0.055$ for 1703 unique reflections. The tridentate dianionic ligand spans three positions in the basal plane, including the phenolic O atom, the neutral N atom and the thiolate S atom, the fourth position being occupied by the benzenethiolate S atom. The Tc atom lies 0.66 Å above the basal plane towards the O(1) apex and with respect to the mean basal plane the four donor atoms are in a slightly puckered (±0.12 Å) arrangement.

Introduction. Neutral Tc complexes TcO(S*X*S)(S*R*), with $^-$S*X*S$^-$ = dianionic tridentate ligands $^-$S—CH_2CH_2—*X*—CH_2CH_2—S$^-$ (*X* = O,S) and *R*S$^-$ = monodentate thiolates were obtained by joint action of both the tridentate and the monodentate

* Systematic name: (benzenethiolato)oxo{2-[(2-sulfidophenyl)-iminomethyl]phenolato-*O,N,S*}technetium(V).

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